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(54) Title: METHOD FOR PREPARING CRYSTALLINE ALUMINOPHOSPHATE MATERIALS USING AZA-POLYCYCLIC TEMPLATING AGENTS			
(57) Abstract			
Molecular sieves, particularly metalloaluminophosphates are prepared using templates derived from a 4-azonia-tricyclo[5.2.n.0 <sup>2,6</sup> ]alkene family of compounds. The templates may be prepared in a series of reaction steps which include a Diels-Alder reaction between a diene and a dienophile.			

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01   METHOD FOR PREPARING CRYSTALLINE ALUMINOPHOSPHATE MATERIALS  
02   USING AZA-POLYCYCLIC TEMPLATING AGENTS

03

04   BACKGROUND OF THE INVENTION

05

06   Field of the Invention

07

08   The present invention relates to a new method for  
09   synthesizing crystalline molecular sieves using a family of  
10   templating agents.

11

12   Background

13

14   The crystalline materials of this invention contain metallic  
15   and non-metallic oxides bonded through oxygen linkages to  
16   form a three-dimensional structure. Molecular sieves are a  
17   commercially important class of crystalline materials.

18   Natural and synthetic crystalline molecular sieves are  
19   useful as catalysts and adsorbents. They have distinct  
20   crystal structures with ordered pore structures which are  
21   demonstrated by distinct X-ray diffraction patterns. The  
22   crystal structure defines cavities and pores which are  
23   characteristic of the different species. The adsorptive and  
24   catalytic properties of each molecular sieve are determined  
25   in part by the dimensions of its pores and cavities. Thus,  
26   the utility of a particular molecular sieve in a particular  
27   application depends at least partly on its crystal  
28   structure.

29

30   Because of their unique sieving characteristics, as well as  
31   their catalytic properties, molecular sieves are especially  
32   useful in such applications as gas drying and separation and  
33   hydrocarbon conversion. Although many different molecular  
34   sieves have been disclosed, there is a continuing need for

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01 new materials with desirable properties for gas separation  
02 and drying, hydrocarbon and chemical conversions, and other  
03 applications.

04

05 Aluminophosphate molecular sieves containing  $[AlO_2]$  and  $[PO_2]$   
06 units have been disclosed in U.S. Patent No. 4,310,440,  
07 issued January 12, 1982 to Wilson et al.

08 Silicoaluminophosphates having a three-dimensional crystal  
09 framework of  $PO_2^+$ ,  $AlO_2^-$  and  $SiO_2$  tetrahedral units are taught  
10 in U.S. Patent No. 4,440,871, issued April 3, 1984 to Lok  
11 et al. Aluminophosphates containing  $[AlO_2]$  and  $[PO_2]$   
12 structural units, and one or more metals in tetrahedral  
13 coordination with oxygen atoms are disclosed in U.S. Patent  
14 No. 4,567,029, issued January 28, 1986 to Wilson et al. The  
15 '029 reference teaches using the metals magnesium,  
16 manganese, zinc, and cobalt, and uses the nomenclature  
17 "MeAPO" to identify these metal aluminophosphate materials.

18 U.S. Patent No. 4,686,093, issued August 11, 1987 to  
19 Flanigen et al., describes aluminophosphates containing at  
20 least two elements selected from arsenic, beryllium, boron,  
21 chromium, gallium, germanium, lithium and vanadium. U.S.  
22 Patent No. 4,913,799, issued April 3, 1990 to Gortsema  
23 et al., discloses a large number of aluminophosphates for  
24 use in hydrocracking processes. The aluminophosphates of  
25 '799 contain  $[AlO_2]$  and  $[PO_2]$  structural units, and one or  
26 more metals in tetrahedral coordination, including arsenic,  
27 beryllium, boron, chromium, cobalt, gallium, germanium,  
28 iron, lithium, magnesium, manganese, silicon, titanium,  
29 vanadium, and zinc. U.S. Patent No. 4,973,785, issued  
30 November 27, 1990 to Lok et al., expands the list of  
31 aluminophosphates, and teaches the use for converting  
32 hydrocarbons using silicoaluminophosphates containing at  
33 least one element, "EL" capable of forming a three  
34

-3-

01 dimensional oxide framework having a mean "EL---O" distance  
02 in tetrahedral oxide structures between 1.51Å and 2.06Å,  
03 where "EL" has a cation electronegativity between 125 to 310  
04 kcal/g-atom, and is capable of forming stable EL--O--P,  
05 EL--O--Al or El--O--El bonds in crystalline three  
06 dimensional oxide structures having an "EL--O" bond  
07 dissociation energy greater than about 59 kcal/mole at  
08 289°C.

09

10 Organic templating agents are believed to play an important  
11 role in the process of molecular sieve crystallization.  
12 Organic amines and quaternary ammonium cations were first  
13 used in the synthesis of zeolites in the early 1960's. This  
14 approach led to a significant increase in the number of new  
15 zeolitic structures discovered as well as an expansion in  
16 the boundaries of composition of the resultant crystalline  
17 products.

18

19 Unfortunately, the relationship between structure of the  
20 organocation and the resultant zeolite is far from  
21 predictable, as evidenced by the multitude of products which  
22 can be obtained using a single quaternary ammonium salt as  
23 reported by S. I. Zones et al., 1989, *Zeolites: Facts,*  
24 *Figures, Future*, ed. P. A. Jacobs and R. A. van Santen,  
25 pp. 299-309, Amsterdam: Elsevier Science Publishers., or the  
26 multitude of organocations which can produce a single  
27 zeolitic product as reported by R. M. Barrer, 1989, *Zeolite*  
28 *Synthesis*, ACS Symposium 398, ed. M. L. Occelli and H. E.  
29 Robson, pp. 11-27, American Chemical Society.

30

31 Thus, it is known that organocations exert influence on the  
32 molecular sieve crystallization processes in many  
33 unpredictable ways. Aside from acting in a templating role,  
34 the organic cation's presence also greatly affects the

-4-

01 characteristics of the gel. These effects can range from  
02 modifying the gel pH to altering the interactions of the  
03 various components via changes in hydration (and thus  
04 solubilities of reagents) and other physical properties of  
05 the gel. Accordingly, investigators have now begun to  
06 consider how the presence of a particular quaternary  
07 ammonium salt influences many of these gel characteristics  
08 in order to determine more rigorously how such salts exert  
09 their templating effects.

10

11 It has been noted that many of the organocations which have  
12 been used as templates for zeolite synthesis are  
13 conformationally flexible. These molecules can adopt many  
14 conformations in aqueous solution, therefore several  
15 templates can give rise to a particular crystalline product.  
16 Studies which involved alterations on such conformationally  
17 flexible organic amines and cations have been published.  
18 For example, one study, Rollmann and Valyocsik, 1985,  
19 Zeolites 5, 123, describes how varying the chain length for  
20 a series of  $\alpha,\omega$ -linear diamines resulted in different  
21 intermediate-pore products. It has also been recently  
22 reported by M. D. Shannon et al., 1991, Nature 353, 417-420  
23 and J. L. Casci, 1986, *New Developments in Zeolite Science*  
24 and *Technology*, ed. Y. Murakami et al., pp. 215-222,  
25 Elsevier that three different products which have related  
26 framework topologies, can be formed from three linear  
27 bis-quaternary ammonium templates of varying chain lengths.  
28

29

30 Altering the structure of a conformationally rigid organic  
31 molecule can also lead to a change in the zeolite obtained,  
32 presumably due to the differing steric demands of each  
33 template. S. I. Zones, 1989, Zeolites 9, 458-467 reported  
34 that in switching from 1,3-dimethylimidazolium hydroxide to  
1,3-diisopropylimidazolium hydroxide as template, using the

-5-

01 same starting gel ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ ), the former directs  
02 toward formation of ZSM-22 whereas the latter affords  
03 ZSM-23.

04

05 In summary, a variety of templates have been used to  
06 synthesize a variety of molecular sieves, including  
07 zeolites, aluminophosphates, and silicoaluminophosphates.  
08 Though the specific utility of a given template is at  
09 present unpredictable, a few notable cyclic-organocation  
10 templating agents have been reported. For instance, use of  
11 N,N,N-trimethyl cyclopentylammonium iodide in the  
12 preparation of Zeolite SSZ-15 molecular sieve is disclosed  
13 in U.S. Patent No. 4,610,854, issued September 9, 1986 to  
14 Zones; use of 1-azoniaspiro [4.4] nonyl bromide and  
15 preparation of a molecular sieve termed "Losod" is disclosed  
16 in *Hel. Chim. Acta* (1974), Vol. 57, page 1533 (W. Sieber and  
17 W. M. Meier); use of 1, $\omega$ -di(1-azoniabicyclo [2.2.2.] octane)  
18 lower alkyl compounds in the preparation of Zeolite SSZ-16  
19 molecular sieve is disclosed in U.S. Patent No. 4,508,837,  
20 issued April 2, 1985 to Zones; use of N,N,N-trialkyl-1  
21 adamant ammonium salts in the preparation of zeolite SSZ-13  
22 molecular sieve is disclosed in U.S. Patent No. 4,544,538,  
23 issued October 1, 1985 to Zones. U.S. Patent No. 5,053,373,  
24 issued October 1, 1991 to Zones discloses preparing SSZ-32  
25 with an N-lower alkyl-N'-isopropyl-imidazolium cation  
26 templating agent. U.S. Patent No. 5,106,801, issued April  
27 21, 1992 to Zones et al. discloses a cyclic quaternary  
28 ammonium ion, and specifically a tricyclodecane quaternary  
29 ammonium ion, for the preparation of the metallosilicate  
30 zeolite SSZ-31. U.S. Patent No. 4,910,006, issued March 20,  
31 1990 to Zones et al., teaches using a  
32 hexamethyl[4.3.3.0]propellane-8,11-diammonium cation for the  
33 preparation of SSZ-26. EP 0193282 discloses a tropinium  
34 cation for preparing the clathrasil ZSM-58. Similarly, use

01 of quinuclidinium compounds to prepare a zeolite termed  
02 "NU-3" is disclosed in European Patent Publication  
03 No. 40016.

04

05 The use of 1,4-diazabicyclo[2.2.2]octane; N,N'-dimethyl-1,4  
06 diazabicyclo[2.2.2]octane dihydroxide; and quinuclidine are  
07 examples of amines taught in U.S. Patent No. 4,310,440,  
08 issued January 12, 1982 to Wilson et al., and U.S. Patent  
09 No. 4,440,871, issued April 3, 1984 to Lok et al. for the  
10 preparation of aluminophosphates and silicoaluminophosphates  
11 respectively.

12

13 SUMMARY OF THE INVENTION

14

15 This invention provides a novel process for preparing  
16 crystalline materials, particularly molecular sieves having  
17 framework structures comprising [AlO<sub>2</sub>] and [PO<sub>2</sub>] units. This  
18 process includes contacting active sources of the components  
19 of the crystalline materials with an organocationic  
20 templating agent which is derived from a  
21 4-azonia-tricyclo[5.2.n.0<sup>2,6</sup>]alkene family of compounds,  
22 wherein each member of the family is a compound which may be  
23 prepared via a Diels-Alder reaction pathway.

24

25 More specifically, a method is provided for preparing a  
26 crystalline molecular sieve comprising oxides of one or more  
27 trivalent element(s) and oxides of one or more pentavalent  
28 element(s), said method comprising contacting under  
29 crystallization conditions one or more active sources of  
30 said oxides with a templating agent having a molecular  
31 structure of the form:

32

33

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-7-

01 (I)

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11

12 (IA)

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14

15

16

17 wherein:

18

19 R<sub>1</sub> and R<sub>2</sub> are at each independent occurrence selected  
20 from the group consisting of hydrogen, a lower alkyl  
21 group, and when taken together, a spirocyclic group  
22 having from 3 to 6 carbon atoms;

23

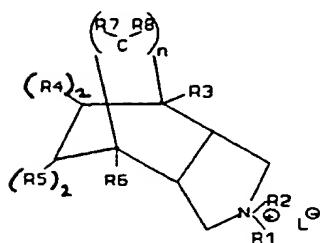
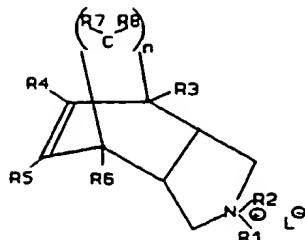
24 R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> are at each independent occurrence  
25 selected from the group consisting of hydrogen,  
26 halogen, and a lower alkyl group;

27

28 n has at each independent occurrence a value of 1, 2,  
29 3, or 4;

30

31 R<sub>7</sub> and R<sub>8</sub> are at each independent occurrence selected  
32 from the group consisting of hydrogen and a lower alkyl  
33 group, and when n is one (1), R<sub>7</sub> and R<sub>8</sub> can be taken  
34 together to form a spirocyclic group having from 3 to 6



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01       carbon atoms; and when n is two (2) or greater, one of  
02       R7 and R8 on one carbon atom can be taken together with  
03       one of R7 and R8 on an adjacent carbon atom to form a  
04       ring having from 3 to 6 carbon atoms; and  
05

06       L is an anion which is not detrimental to the formation  
07       of the molecular sieve, such as anions including  
08       halogens, such as fluoride, chloride, bromide, and  
09       iodide, hydroxide, acetate, sulfate, carboxylate, with  
10       hydroxide being most preferred, or a molecular  
11       structure of the form:

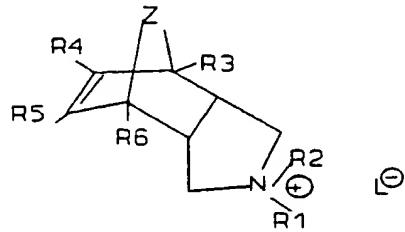
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16       (II)



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18

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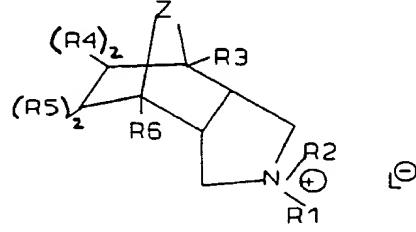
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23

24       (IIA)



25

26

27

28

29       wherein:

30

31       Z is at each independent occurrence selected from the  
32       group consisting of oxygen, nitrogen, sulfur, and a  
33       hydrocarbyl (e.g., alkylene, alkylidene, substituted  
34

-9-

01                 alkylene and the like having 1 to about 6 carbon atoms)  
02                 radical; and  
03  
04                 R1, R2, R3, R4, R5, R6, and L are as defined above.  
05  
06                 Aza-polycyclic compounds encompassed by this formula are  
07                 hereinafter referred to as the "defined aza-polycyclic  
08                 templating agents".  
09  
10                 The molecular sieve of this invention has a three-  
11                 dimensional microporous framework structure comprising  
12                 [AlO<sub>2</sub>] and [PO<sub>2</sub>] oxide units. The molecular sieve may  
13                 additionally comprise an oxide of at least one element other  
14                 than aluminum and phosphorous which is capable of forming an  
15                 oxide in tetrahedral coordination with [AlO<sub>2</sub>] and [PO<sub>2</sub>] oxide  
16                 structural units in the molecular sieve. The preferred  
17                 elements other than aluminum and phosphorous are selected  
18                 from the group consisting of arsenic, beryllium, boron,  
19                 chromium, cobalt, gallium, germanium, iron, lithium,  
20                 magnesium, manganese, silicon, titanium, vanadium, and zinc.  
21                 Silicon, magnesium, manganese, cobalt, and zinc are more  
22                 preferred, with silicon being particularly preferred.  
23  
24                 The present invention is also directed to a crystalline  
25                 molecular sieve comprising oxides of one or more trivalent  
26                 element(s) and of one or more pentavalent element(s), and  
27                 having therein the defined aza-polycyclic templating agent.  
28  
29                 Preferably, the molecular sieve has a molar composition, as  
30                 synthesized and in the anhydrous state, as follows:  
31  
32                 aQ: (M<sub>x</sub>Al<sub>y</sub>P<sub>z</sub>)O<sub>2</sub>  
33  
34                 wherein:

-10-

01       Q is the defined aza-polycyclic templating agent having  
02       a molecular structure of the form shown in Structure I,  
03       IA, II or IIIA above;

04

05       a has a value in the range of greater than zero and no  
06       greater than about 0.3;

07

08       M is one or more elements capable of forming stable  
09       M--O--P, M--O--Al, or M--O--M bonds in crystalline  
10       oxide structures;

11

12       y and z each have a value of at least 0.01; and

13

14       the sum of x, y, and z is 1.

15

16       Among other factors, the present invention is based on the  
17       discovery that small changes in structure within this family  
18       of relatively rigid, polycyclic templating agents, when the  
19       template is used in molecular sieve synthesis, can lead to  
20       significant changes in the crystalline molecular sieve  
21       formed.

22

23       DETAILED DESCRIPTION OF THE INVENTION

24

25       In preparing a crystalline material according to the present  
26       invention, a defined aza-polycyclic compound, having a  
27       general molecular structure of the form shown in Structure I  
28       above, acts as a template or structure directing agent  
29       during the crystallization. Typically, the defined  
30       aza-polycyclic templating agent is prepared in a series of  
31       reaction steps comprising a Diels-Alder reaction between a  
32       diene and a dienophile.

33

34

-11-

01 In another embodiment is the molecular sieve, in its  
02 as-synthesized form containing the defined aza-polycyclic  
03 templating agent.

04

05 In the method of this invention the family of aza-polycyclic  
06 cations can be used to synthesize different aluminophosphate  
07 materials depending on the reagents, reactant ratios and  
08 reaction conditions. For example, factors which may affect  
09 the crystallization of a given aluminophosphate include the  
10 specific defined aza-polycyclic template used, the type and  
11 ratio of inorganic reagents used, the methods used in mixing  
12 reagents and the temperature and time used in  
13 crystallization.

14

15 The full scope of the composition and process of the present  
16 invention will be apparent to those familiar with  
17 crystalline molecular sieves and their methods of  
18 preparation from the following detailed description of the  
19 principal features of the composition and from the examples  
20 which accompany the description.

21

22 The Templating Agent

23

24 The templating agents useful in the present process are  
25 derived from the 4-azonia-tricyclo[5.2.n.0<sup>2,6</sup>]alkene family  
26 of compounds, where n is a number and has a value of 1, 2,  
27 3, or 4. The templating agent has a molecular structure of  
28 the general form:

29

30

31

32

33

34

-12-

01 (I)

02

03

04

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10

11

12 (IA)

13

14

15

16

17 wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, L and n are as  
18 defined above.

19

20 The templating agent may also have a molecular structure of  
21 the general form:

22

23

24 (II)

25

26

27

28

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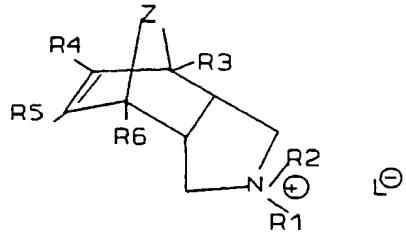
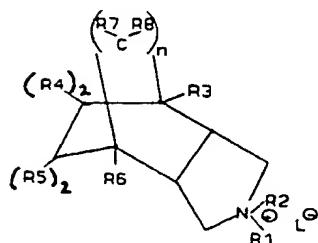
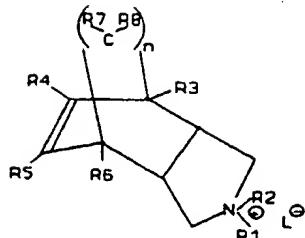
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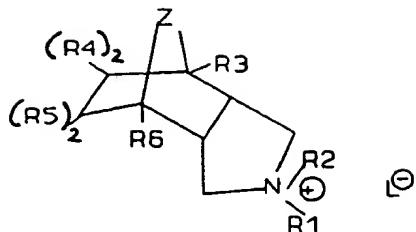
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01  
02  
03  
04 (IIA)  
05  
06  
07  
08



09 wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, Z and L are as defined  
10 above.

11 Preferably, R<sub>1</sub> and R<sub>2</sub> are each selected from the group  
12 consisting of hydrogen, an alkyl group having from 1 to 3  
13 carbon atoms, and when taken together, a spirocyclic group  
14 having from 3 to 6, more preferably from 4 to 5, carbon  
15 atoms.

16  
17 Preferably, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> are each selected from the  
18 group consisting of hydrogen, halogen, and an alkyl group  
19 having from 1 to 3 carbon atoms.

20  
21 Preferably, R<sub>7</sub> and R<sub>8</sub> are each selected from the group  
22 consisting of hydrogen and an alkyl group having from 1 to 3  
23 carbon atoms, and when n is one (1), R<sub>7</sub> and R<sub>8</sub> can be taken  
24 together to form a spirocyclic group having from 3 to 6,  
25 more preferably from 3 to 5, carbon atoms; and when n is two  
26 (2) or greater, one of R<sub>7</sub> and R<sub>8</sub> on one carbon atom can be  
27 taken together with one of R<sub>7</sub> and R<sub>8</sub> on an adjacent carbon  
28 atom to form a ring having from 3 to 6, more preferably from  
29 3 to 5, carbon atoms.

30  
31 As used herein, the term "halogen" refers to fluorine,  
32 chlorine, bromine, iodine and combinations thereof. The  
33 term "lower alkyl group" refers to a linear, branched, or  
34 cyclic alkyl group having from 1 to 6 carbon atoms. The

01 term "spirocyclic group" refers to a cyclic group in a  
02 polycyclic hydrocarbon having one carbon atom in common with  
03 a second cyclic group. L is an anion which is not  
04 detrimental to the formation of the molecular sieve.  
05 Representative anions include halogens, such as fluoride,  
06 chloride, bromide, and iodide, hydroxide, acetate, sulfate,  
07 carboxylate. Hydroxide is the most preferred anion. It may  
08 be beneficial to ion exchange, for example, the halide for  
09 hydroxide ion, thereby reducing or eliminating the alkali  
10 metal hydroxide quantity required.

11

12 Many of the organocations which have been previously used as  
13 templates for molecular sieve synthesis are conformationally  
14 flexible. These molecules adopt many conformations in  
15 aqueous solution, and several templates can give rise to a  
16 single crystalline product. In contrast, the defined  
17 aza-polycyclic templating agents used in the present  
18 invention are conformationally rigid organic molecules.  
19 Altering the structure of these rigid molecules can lead to  
20 a change in the molecular sieve obtained, presumably due to  
21 the differing steric demands of each template. In  
22 particular, it has been found that the present templating  
23 agents are useful for synthesizing large pore molecular  
24 sieves, which are important for certain catalytic  
25 applications.

26

27 Increasing the steric demand of the template may lead to a  
28 decrease in crystallization rate as well as a decrease in  
29 template solubility in the reaction mixture. If the  
30 template is not sufficiently soluble, it will be difficult  
31 to form crystals in the reaction mixture. Addition of a  
32 surfactant to the reaction mixture may help to solubilize  
33 the template.

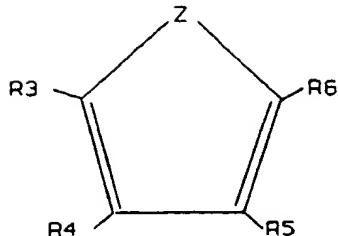
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-15-

01 Employing a Diels-Alder reaction scheme, using inexpensive  
02 reagents, is the preferred method for preparing the present  
03 templating agents. The Diels-Alder reaction is one of the  
04 most useful transformations in synthetic organic chemistry.  
05 Two new bonds and a six-membered ring are formed in the  
06 Diels-Alder reaction, formally a [4+2]cycloaddition of a  
07 1,4-conjugated diene with a double bond (dienophile). The  
08 dienophile may include a carbon-carbon, carbon-heteroatom,  
09 or heteroatom-heteroatom double (or triple) bond, leading to  
10 a diverse pool of potential templating agents. Electron-  
11 withdrawing groups on the dienophile greatly increase its  
12 reactivity, whereas electron-donating groups on the diene  
13 have the same effect. The Diels-Alder reaction is discussed  
14 in greater detail in F. Fringuelli and A. Taticchi, *Dienes*  
15 in the *Diels-Alder Reaction 1990*, J. Wiley and Sons, Inc.  
16  
17 The versatility of the Diels-Alder reaction is in part  
18 responsible for its usefulness. A wide range of starting  
19 materials are available, making possible the preparation of  
20 numerous products. The stereoelectronics of the reaction,  
21 as well as its concerted nature, often allows one to predict  
22 which product will be formed if several are possible.  
23 Therefore, by the proper choice of starting materials, very  
24 efficient syntheses of target templates can be achieved.  
25  
26 In particular, the Diels-Alder reaction pathway provides a  
27 method for synthesizing the defined aza-polycyclic ring  
28 systems which are useful in the present process. Varying  
29 either the diene or the dienophile produces small but  
30 significant structural changes to the key intermediates in  
31 the synthesis.  
32  
33 The dienes useful for preparing the defined aza-polycyclic  
34 templates are of the following general form:

-16-

01  
02  
03  
04 (III)  
05  
06  
07



08 wherein R3, R4, R5, R6, and Z are as defined above.

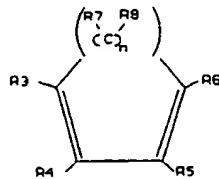
09

10 In a further embodiment, the dienes useful for preparing the  
11 defined aza-polycyclic templates have the following form:

12

13

14  
15  
16 (IV)  
17



18 wherein R3, R4, R5, R6, R7, R8, and n are as defined above.

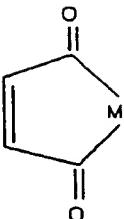
19

20 Examples of cyclic dienes having a carbon backbone include  
21 cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene,  
22 1,3-cycloheptatriene, spiro[2,4]hepta-4,6-diene, and  
23 1,3-cyclooctadiene. The diene of Structure III may also  
24 include one or more heteroatoms in the cyclic backbone,  
25 including oxygen, nitrogen, and/or sulfur. Oxygen is  
26 preferred. Non-limiting examples of heterodienes which are  
27 used in preparing the templating agent include furan,  
28 pyrrol, and thiophene. Examples of functional groups R7 and  
29 R8 in Structure IV are hydrogen, methyl, ethyl, propyl, and  
30 cyclopropyl.

31

32 The dienophile from which the present templating agent is  
33 prepared has a structure of the general form:

01  
02  
03  
04 (V)  
05  
06  
07



08 wherein X is either oxygen or nitrogen having a substituent  
09 group selected from the group consisting of hydrogen and a  
10 lower alkyl group.

11  
12 The defined aza-polycyclic compounds are prepared by methods  
13 known in the art. The reactions involved are described in  
14 detail in, for example, *Chem. Pharm. Bull.* (1962), 10,  
15 714-718, L. F. Fieser and M. Fieser, 1967, *Reagents for*  
16 *Organic Synthesis*, vol 1, pp. 581-594, New York: J. Wiley  
17 and Sons, Inc. and W. K. Anderson and A. S. Milowsky, 1985,  
18 *J. Org. Chem.* 50, 5423-24. When a diene, such as that shown  
19 in Structure IV above, is reacted with a dienophile such as  
20 that shown in Structure V, element M is oxygen, the  
21 resulting product is reacted with an amine to form an imide,  
22 then reduced to the corresponding pyrrolidine using a  
23 reducing agent such as lithium aluminum hydride, and then  
24 quaternized with, for example methyl iodide, to form the  
25 defined aza-polycyclic templating agent.

26  
27 When the diene of Structure III or IV above, is reacted with  
28 a dienophile of Structure V, wherein element M is nitrogen  
29 having a lower alkyl substituent group, the resulting imide  
30 product is directly reduced to the corresponding pyrrolidine  
31 and then quaternized to form the cationic templating agent.

32  
33 The double bond shown in Structures I and II above is not  
34 critical to the action of the defined aza-polycyclic

-18-

01 compound as a templating agent, and may be reduced, using  
02 techniques readily available in the art, such as, for  
03 example, by reaction over a palladium/carbon or a  
04 platinum/carbon catalyst in the presence of hydrogen. The  
05 reduced compound will also serve as a templating agent in  
06 the present method.

07

08 The Reaction Mixture

09

10 The molecular sieves of this invention can be prepared from  
11 an aqueous solution comprising sources of one or more  
12 trivalent elements, one or more pentavalent elements and the  
13 defined aza-polycyclic templating agents of this invention.  
14 Typically, the trivalent element will be aluminum and the  
15 pentavalent element will be phosphorus. The reaction  
16 mixture may optionally contain sources of another element(s) (M)  
17 capable of forming stable M--O--P, M--O--Al or M--O--P bonds  
18 in the molecular sieve crystalline oxide structure.

19

20 In general, the reaction mixture should have a composition,  
21 in terms of mole ratios of oxides, within the ranges shown  
22 below. For convenience, aluminum has been used as the  
23 trivalent element and phosphorus as the pentavalent element,  
24 but it is not intended that the tri- and pentavalent  
25 elements be limited to those elements.

26

27  $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0-0.2 \text{ MO}_2 : 0.5 \text{ Q}_2\text{O} : 120-140 \text{ H}_2\text{O}$

28

29 where M is the element (typically silicon) capable of  
30 forming the stable M--O--Al, M--O--P or M--O--M bonds, and Q  
31 is the defined aza-polycyclic templating agent.

32

33

34

-19-

01           Crystalline Materials of this Invention

02

03       The crystalline material of this invention comprises the  
04       defined aza-polycyclic templating agent in combination with  
05       one or more metallic and/or non-metallic oxides bonded in  
06       tetrahedral coordination through shared oxygen atoms to form  
07       a cross-linked three dimensional crystal structure. The  
08       metallic and non-metallic oxides comprise one or more  
09       trivalent element(s) and one or more pentavalent element(s).  
10       The trivalent element is preferably aluminum and the  
11       pentavalent element is preferably phosphorous. The entire  
12       lattice is charge balanced.

13

14       The term "molecular sieve" refers to a material prepared  
15       according to the present invention having a fixed,  
16       open-network structure, usually crystalline, that may be  
17       used to separate hydrocarbons or other mixtures by selective  
18       occlusion of one or more of the constituents, or may be used  
19       as a catalyst in a catalytic conversion process.

20

21       The term "metalloaluminophosphate" encompasses crystalline  
22       molecular sieves comprising tetrahedrally-bound  $[AlO_2]$  and  
23        $[PO_2]$  oxide structural units. Examples include crystalline  
24       aluminophosphates having a chemical composition, in oxide  
25       mole ratios, of  $Al_2O_3:1.0\pm0.2 P_2O_5$ . Optionally, the  
26       crystalline metalloaluminophosphate may further comprise, in  
27       addition to aluminum and phosphorous, tetrahedrally-bound  
28       oxide units of one or more elements which are capable of  
29       forming tetrahedral oxide units with the  $[AlO_2]$  and  $[PO_2]$   
30       units, including arsenic, beryllium, boron, chromium,  
31       cobalt, gallium, germanium, iron, lithium, magnesium,  
32       manganese, silicon, titanium, vanadium, and zinc.

33

34

-20-

01   Typically, the crystalline material has a molar composition,  
02   as synthesized and in the anhydrous state, as follows:

03

04            aQ:  $(M_xAl_yP_z)O_2$

05

06   wherein:

07

08       Q is the defined aza-polycyclic templating agent having  
09       a molecular structure of the form shown in Structure I,  
10       IA, II or IIIA above;

11

12       a has a value in the range of greater than zero and no  
13       greater than about 0.3;

14

15       M is one or more elements capable of forming stable  
16       M--O--P, M--O--Al, or M--O--M bonds in crystalline  
17       oxide structures;

18

19       y and z each have a value of at least 0.01; and

20

21       the sum of x, y, and z is 1.

22

23       The crystalline material can be suitably prepared from an  
24       aqueous solution containing at least one defined  
25       aza-polycyclic templating agent, and sources of at least one  
26       oxide capable of forming a crystalline molecular sieve.  
27       Examples of a suitable metal oxide include an alkali metal  
28       oxide, and oxides of aluminum, silicon, boron, germanium,  
29       iron, gallium, phosphorous, arsenic, beryllium, chromium,  
30       cobalt, gallium, magnesium, manganese, titanium, vanadium,  
31       and zinc.

32

33       The present process is suitable for preparing a  
34       metalloaluminophosphate molecular sieve from a reaction

-21-

01 mixture prepared using standard preparation techniques.  
02 Aluminophosphates and the conventional preparation thereof  
03 are described in U.S. Patent No. 4,310,440, issued  
04 January 12, 1982 to Wilson et al., the disclosure of which  
05 is incorporated herein by reference.  
06 Silicoaluminophosphates and the conventional preparation  
07 thereof are described in U.S. Patent No. 4,440,871, issued  
08 April 3, 1984 to Lok et al., and U.S. Patent No. 4,943,424,  
09 issued July 24, 1990 to Miller, the disclosures of which are  
10 incorporated herein by reference. Metalloaluminophosphates  
11 and the convention preparation thereof are described in U.S.  
12 Patent No. 4,913,799, issued April 30, 1990 to Gortsema  
13 et al., the disclosure of which is incorporated by  
14 reference. In the '799 patent the metalloaluminophosphates  
15 are termed "non-zeolitic molecular sieve".  
16  
17 The preferred source of aluminum for the crystalline  
18 aluminophosphate and metal aluminophosphate molecular sieves  
19 of this invention is an aluminum alkoxide such as aluminum  
20 isopropoxide or pseudo-boehmite. Phosphoric acid is the  
21 preferred source of phosphorous. Organic phosphates and  
22 crystalline aluminophosphates can also be employed as a  
23 source of phosphorous. Typical sources of silicon oxide  
24 include silicates, silica hydrogel, silicic acid, colloidal  
25 silica, tetra-alkyl orthosilicates, and silica hydroxides.  
26 Sources of the other oxides typically include salts which  
27 are soluble in the reaction mixture.  
28  
29 In preparing the crystalline material under crystallization  
30 conditions according to the present invention, the reaction  
31 mixture is maintained under hydrothermal conditions at an  
32 elevated temperature until crystals are formed. The  
33 temperatures during the hydrothermal crystallization step  
34 are typically maintained from about 50°C to about 200°C.

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01      The crystallization period is typically greater than 1 day  
02      and preferably from about 3 days to about 50 days.

03

04      The hydrothermal crystallization is usually conducted under  
05      pressure and usually in an autoclave so that the reaction  
06      mixture is subject to autogenous pressure. The reaction  
07      mixture can be stirred during crystallization.

08

09      More specifically, the synthesis method for preparing  
10      metalloaluminophosphates comprises:

11

12            (a) preparing an aqueous reaction mixture containing  
13               aluminum isopropoxide and phosphoric acid,  
14               thereafter combining the aqueous reaction mixture  
15               with an organic templating agent and optionally  
16               adding active source(s) of one or more additional  
17               elements capable of forming oxides in tetrahedral  
18               coordination with  $[AlO_4]$  and  $[PO_4]$  units, to form  
19               the complete reaction mixture in the relationship  
20               herein before set forth;

21

22            (b) heating the complete reaction mixture to a  
23               temperature in the range of from 50°C to 240°C and  
24               preferably from 100°C to 200°C until crystals are  
25               formed, usually from 5 hours to 500 hours and  
26               preferably 24 to 480 hours; and

27

28            (c) recovering the crystalline product.

29

30      Once the crystals have formed, the solid product is  
31      separated from the reaction mixture by standard mechanical  
32      separation techniques, such as filtration. The crystals are  
33      water-washed and then dried, e.g., at 90°C to 150°C for from  
34      8 to 24 hours, to obtain the synthesized zeolite crystals.

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01      The drying step can be performed at atmospheric or  
02      subatmospheric pressures.

03

04      During the hydrothermal crystallization step, the crystals  
05      can be allowed to nucleate spontaneously from the reaction  
06      mixture. The reaction mixture can also be seeded with  
07      crystals both to direct, and accelerate the crystallization,  
08      as well as to minimize the formation of undesired  
09      contaminants. If the reaction mixture is seeded with  
10      crystals, the concentration of the defined aza-polycyclic  
11      template may sometimes be somewhat reduced.

12

13      Due to the unpredictability of the factors which control  
14      nucleation and crystallization in the art of crystalline  
15      oxide synthesis, not every combination of reagents, reactant  
16      ratios, and reaction conditions will result in crystalline  
17      products. Selecting crystallization conditions which are  
18      effective for producing crystals may require routine  
19      modifications to the reaction mixture composition or to the  
20      reaction conditions, such as temperature and/or  
21      crystallization time. Making these modifications are well  
22      within the capabilities of one skilled in the art.

23

24      The crystalline material can be thermally treated  
25      (calcined). Usually, it is desirable to remove the alkali  
26      metal cation by ion exchange and replace it with hydrogen,  
27      ammonium, or any desired metal ion. The molecular sieve can  
28      be leached with chelating agents, e.g., EDTA or dilute acid  
29      solutions, to increase the silica/alumina mole ratio. The  
30      molecular sieve can also be steamed; steaming helps  
31      stabilize the crystalline lattice to attack from acids. The  
32      molecular sieve can be used in intimate combination with  
33      hydrogenating components, such as tungsten, vanadium  
34      molybdenum, rhenium, nickel cobalt, chromium, manganese, or

01 a noble metal, such as palladium or platinum, for those  
02 applications in which a hydrogenation-dehydrogenation  
03 function is desired. Typical replacing cations can include  
04 metal cations, e.g., rare earth, Group IIA and Group VIII  
05 metals, as well as their mixtures. Of the replacing  
06 metallic cations, cations of metals such as rare earth, Mn,  
07 Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are  
08 particularly preferred.

09

10 The hydrogen, ammonium, and metal components can be  
11 exchanged into the zeolite. The molecular sieve can also be  
12 impregnated with the metals, or, the metals can be  
13 physically intimately admixed with the molecular sieve using  
14 standard methods known to the art. The metals can also be  
15 occluded in the crystal lattice by having the desired metals  
16 present as ions in the reaction mixture from which the  
17 molecular sieve is prepared.

18

19 Typical ion exchange techniques involve contacting the  
20 synthetic molecular sieve with a solution containing a salt  
21 of the desired replacing cation or cations. Although a wide  
22 variety of salts can be employed, chlorides and other  
23 halides, nitrates, and sulfates are particularly preferred.  
24 Representative ion exchange techniques are disclosed in a  
25 wide variety of patents including U.S. Patent  
26 Nos. 3,140,249, issued July 7, 1964 to Plank et al.;  
27 3,140,251, issued July 7, 1964 to Plank et al.; and  
28 3,140,253, issued July 7, 1964 to Plank et al. Ion exchange  
29 can take place before or after the zeolite is calcined.

30

31 Following contact with the salt solution of the desired  
32 replacing cation, the zeolite is typically washed with water  
33 and dried at temperatures ranging from 65°C to about 315°C.  
34 After washing, the molecular sieve can be calcined in air or

-25-

01 inert gas at temperatures ranging from about 200°C to about  
02 800°C for periods of time ranging from 1 to 48 hours, or  
03 more, to produce a catalytically active product especially  
04 useful in hydrocarbon conversion processes.

05

06 Regardless of the cations present in the synthesized form of  
07 the molecular sieve, the spatial arrangement of the atoms  
08 which form the basic crystal lattice of the zeolite remains  
09 essentially unchanged. The exchange of cations has little,  
10 if any effect on the molecular sieve lattice structures.

11

12 The molecular sieve can be formed into a wide variety of  
13 physical shapes. Generally speaking, the molecular sieve  
14 can be in the form of a powder, a granule, or a molded  
15 product, such as extrudate having a particle size sufficient  
16 to pass through a 2-mesh (Tyler) screen and be retained on a  
17 400-mesh (Tyler) screen. In cases where the catalyst is  
18 molded, such as by extrusion with an organic binder, the  
19 aluminosilicate can be extruded before drying, or, dried or  
20 partially dried and then extruded.

21

22 The molecular sieve can be composited with other materials  
23 resistant to the temperatures and other conditions employed  
24 in organic conversion processes. Such matrix materials  
25 include active and inactive materials and synthetic or  
26 naturally occurring zeolites as well as inorganic materials  
27 such as clays, silica and metal oxides. The latter may be  
28 naturally occurring or may be in the form of gelatinous  
29 precipitates, sols, or gels, including mixtures of silica  
30 and metal oxides. Use of an active material in conjunction  
31 with the synthetic molecular sieve, combined with it, can  
32 improve the conversion and selectivity of the catalyst in  
33 certain organic conversion processes. Inactive materials  
34 can serve as diluents to control the amount of conversion in

01 a given process so that products can be formed economically  
02 without using other means for controlling the rate of  
03 reaction. Frequently, molecular sieve materials have been  
04 incorporated into naturally occurring clays, e.g., bentonite  
05 and kaolin. These materials, i.e., clays, oxides, etc.,  
06 function, in part, as binders for the catalyst. It is  
07 desirable to provide a catalyst having good crush strength  
08 and attrition resistance, because in petroleum refining the  
09 catalyst is often subjected to rough handling. This tends  
10 to break the catalyst down into powders which cause problems  
11 in processing.

12

13 Naturally occurring clays which can be composited with the  
14 synthetic molecular sieves of this invention include the  
15 montmorillonite and kaolin families, which families include  
16 the sub-bentonites and the kaolins commonly known as Dixie,  
17 McNamee, Georgia and Florida clays or others in which the  
18 main mineral constituent is halloysite, kaolinite, dickite,  
19 nacrite, or anauxite. Various clays such as sepiolite and  
20 attapulgite can also be used as supports. Such clays can be  
21 used in the raw state as originally mined or can be  
22 calcined, treated with acid, or chemically modified.

23

24 In addition to the foregoing materials, the molecular sieve  
25 can be composited with porous matrix materials and mixtures  
26 of matrix materials such as silica, alumina, titania,  
27 magnesia, silica-alumina, silica-magnesia, silica-zirconia,  
28 silica-thoria, silica-beryllia, silica-titania, titania-  
29 zirconia as well as ternary compositions such as silica-  
30 alumina-thoria, silica-alumina-zirconia, silica-alumina-  
31 magnesia and silica-magnesia-zirconia. The matrix can be in  
32 the form of a cogel.

33

34

-27-

01 The molecular sieve can also be composited with zeolites  
02 such as synthetic and natural faujasites (e.g., X and Y),  
03 erionites, and mordenites. They can also be composited with  
04 purely synthetic zeolites. The combination of molecular  
05 sieves and zeolites can also be composited in a porous  
06 inorganic matrix.

07

08 The materials prepared in accordance with this invention are  
09 useful as molecular sieves, catalysts and/or catalyst  
10 carriers.

11

12 The following examples demonstrate but do not limit the  
13 present invention.

14

15

EXAMPLES

16

17 Examples 1-11 show that one can make a wide range of  
18 templates using the methodology described above. In each of  
19 Examples 1-11, the anion L may be either I<sup>-</sup> or OH<sup>-</sup>.

20

21

Example 1

22

23

Diels-Alder adduct:

24

25

The diene cyclopentadiene was obtained by cracking  
26 dicyclopentadiene in a 1-L round bottomed flask fitted with  
27 a 30-cm Vigreux column, following the procedure in R. B.  
28 Moffett, 1963, *Organic Syntheses Coll. Vol IV*, ed.  
29 N. Rabjohn, pp. 238-241, New York: J. Wiley and Sons, Inc.  
30 The cyclopentadiene product was distilled from the cracking  
31 vessel and recovered. A 2-L, 3-necked flask was equipped  
32 with a magnetic stir bar, reflux condenser and thermometer.  
33 The flask was charged with cyclopentadiene (295 grams, 4.46  
34 mol) and benzene (1.4 L). The dienophile N-methylmaleimide

-28-

01 (30.1 grams, 0.45 mol) was added at room temperature  
02 (exotherm noted), and the homogeneous yellow solution was  
03 heated to reflux for 24 hours. Thin layer chromatography  
04 (silica, 40% ethyl acetate/hexane) was used to monitor the  
05 disappearance of maleimide. The reaction mixture was  
06 concentrated by rotary evaporation to yield a mixture of oil  
07 and solid products, which was taken up in 200 mL of CH<sub>2</sub>Cl<sub>2</sub>,  
08 and transferred to a separatory funnel. Water (200 mL) was  
09 added and the pH of the aqueous layer adjusted to ≤ 1 using  
10 conc. HCl. The phases were separated and the organic phase  
11 was washed once more with H<sub>2</sub>O (200 mL). After drying over  
12 MgSO<sub>4</sub>, the organic phase was filtered and concentrated to  
13 yield an oil and solid mixture which was recrystallized from  
14 500 mL of hot Et<sub>2</sub>O. The ethereal solution was placed in the  
15 refrigerator overnight and the resulting white crystals of  
16 the Diels-Alder imide were collected by vacuum filtration  
17 and washed with a small amount of cold ether (65.43 grams,  
18 82% yield, mp 103-105°C).  
19

20 Reduction of Diels-Alder imide:

21

22 A 3-L, 3-necked flask was fitted with a mechanical stirrer,  
23 addition funnel and reflux condenser. The Diels-Alder imide  
24 (61.5 grams, 0.35 mol) was dissolved in 495 mL of CH<sub>2</sub>Cl<sub>2</sub> in  
25 the addition funnel. The flask was charged with LiAlH<sub>4</sub>  
26 (41.6 grams, 1.04 mol) and anhydrous Et<sub>2</sub>O (990 mL) and the  
27 system was placed under N<sub>2</sub>. The imide solution was added  
28 slowly to the LiAlH<sub>4</sub> suspension. Gas evolution and an  
29 exotherm were noted. Addition of the imide solution was  
30 complete after approximately 1 hour and the grey  
31 heterogenous solution was allowed to stir under N<sub>2</sub>  
32 overnight. Thin layer chromatography (silica plates, 5%  
33 MeOH/95% CH<sub>2</sub>Cl<sub>2</sub>) indicated the absence of starting material.  
34

01 The reaction was carefully worked up in the following  
02 manner: 38.5 mL of H<sub>2</sub>O was added slowly to the reaction.  
03 Vigorous gas evolution was noted as well as an exotherm.  
04 This step was followed by the cautious addition of 38.5 mL  
05 of 15% aqueous NaOH solution. Another 115 mL of H<sub>2</sub>O was  
06 added and the mixture, which turned from grey to white, was  
07 stirred for 1 hour at room temperature. The solids were  
08 removed by filtration and washed with CH<sub>2</sub>Cl<sub>2</sub>. The aqueous  
09 layer was acidified with conc. HCl to pH ≤ 1 and the  
10 non-basic organic impurities removed in the organic phase.  
11 The aqueous layer was then made basic (pH ≤ 12) with 50%  
12 NaOH and the crude tertiary amine was isolated by extracting  
13 twice with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined and  
14 dried over MgSO<sub>4</sub>. Following filtration, the solution was  
15 concentrated to yield 41.4 g (52%) of the amine, which was  
16 taken directly to the next step. IR and <sup>13</sup>C NMR spectroscopy  
17 could be used to monitor the disappearance of the imide  
18 functionality (1700 cm<sup>-1</sup> and 177.5 ppm, respectively).  
19

20 Quaternization of the  
21 4-Methyl-4-aza-tricyclo[5.2.1.0]dec-8-ene:  
22

23 The amine (15.0 grams, 0.10 mol) was dissolved in 100 mL of  
24 CHCl<sub>3</sub> in a 250-mL round-bottomed flask which was equipped  
25 with an addition funnel and magnetic stirrer. The reaction  
26 flask was immersed in an ice bath and the addition funnel  
27 charged with CH<sub>3</sub>I (28.7 grams, 0.20 mol). The CH<sub>3</sub>I was added  
28 to the amine over a 10-minute period (exothermic reaction)  
29 and the homogeneous solution was stirred at room temperature  
30 for 3 days. Diethyl ether (100 mL) was added to the  
31 reaction mixture and the yellow solids were collected by  
32 filtration and washed with more ether. These solids were  
33 recrystallized from hot acetone/Et<sub>2</sub>O (a small amount of MeOH  
34

-30-

01 was added to aid in dissolution of solid) to afford  
02 21.2 grams of an aza-polycyclic compound having an iodide  
03 anion. Bio-Rad AG1-X8 anion exchange resin was used to  
04 convert the iodide salt to the corresponding hydroxide form  
05 in 90.5% yield. The yield of the conversion was based upon  
06 titration of the resultant solution using phenolphthalein as  
07 the indicator.

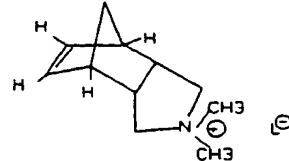
08

09 The aza-polycyclic templating agent of Example 1 had the  
10 structure shown below.

11

12

13  
14 (VI)



15

16

Example 2

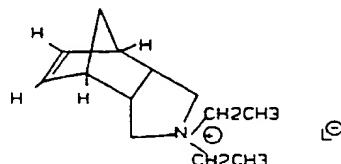
17

18  
19 Example 1 was repeated, except N-ethylmaleimide was used as  
20 the dienophile and CH<sub>3</sub>CH<sub>2</sub>I was used instead of CH<sub>3</sub>I in the  
21 quaternization step. The resulting product had the  
22 structure of Structure VII below, with the alkyl groups  
23 surrounding the positively charged nitrogen being ethyl  
24 rather than methyl.

25

26

27  
28 (VII)



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01

Example 3

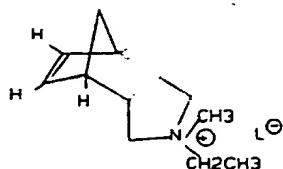
02

03 Example 2 was repeated, except  $\text{CH}_3\text{I}$  was used in the  
04 quaternization step, giving a cationic templating agent  
05 Structure VIII.

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08  
09 (VIII)



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Example 4

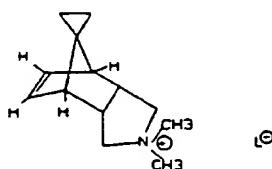
14

15 Example 1 was repeated, except spiro[2.4]hepta-4,6-diene was  
16 used as the diene;  $\text{AlCl}_3$  was used as a Lewis acid, and the  
17 reaction was not heated. In the resulting Structure IX the  
18 bridging carbon is part of a spirocyclic cyclopropyl group.

19

20

21  
22 (IX)



23

24

25

Example 5

26

27 Example 4 was repeated, except N-ethylmaleimide was used as  
28 the dienophile and  $\text{CH}_3\text{CH}_2\text{I}$  was used instead of  $\text{CH}_3\text{I}$  in the  
29 quaternization step, to give Structure X.

30

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-32-

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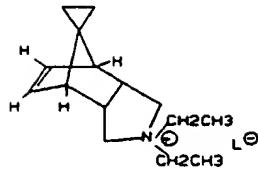
04 (X)

05

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07

08

Example 6

09

Example 1 . . . repeated, except 1,3-cyclohexadiene was used as the diene and toluene was used as the solvent. In the resulting Structure XI the bridging radical has been expanded from one to two carbon atoms.

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14

15

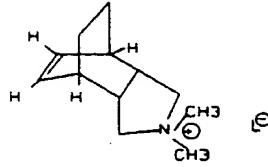
16 (XI)

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Example 7

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27 (XII)

28

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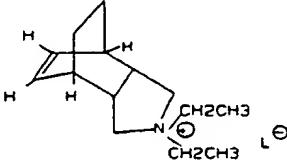
30

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Example 8

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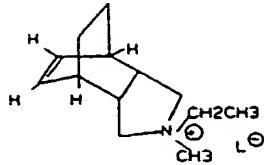
33

34

Example 7 was repeated, except CH<sub>3</sub>I was used in the quaternization step to give Structure XIII.

-33-

01  
02  
03 (XIII)



04  
05  
06

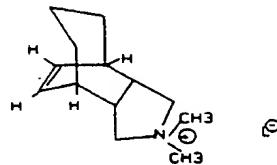
Example 9

07

08 Example 6 was repeated, except 1-3,cycloheptadiene was used  
09 as the diene, and the reaction was heated for four (4) days  
10 to give Structure XIV.

11  
12  
13

14  
15  
16 (XIV)



17  
18

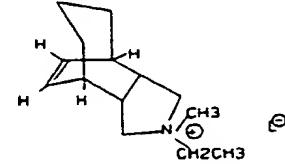
Example 10

19

20 Example 9 was repeated, except CH<sub>3</sub>CH<sub>2</sub>I was used instead of  
21 CH<sub>3</sub>I in the quaternization step to give Structure XV.

22

23  
24  
25  
26 (XV)



27  
28

Example 11

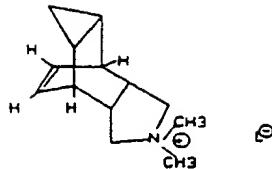
29

30 Example 6 was repeated, except cycloheptatriene was used as  
31 the diene to give Structure XVI.

32  
33  
34

-34-

01  
02  
03 (XVI)  
04  
05



06 Examples 12-20 illustrate using templates of this invention  
07 under a variety of inorganic conditions to obtain  
08 crystalline products. These non-limiting examples  
09 illustrate preferred conditions of the invention.  
10

11 It can be seen that one of the desirable features of this  
12 invention is that a wide variety of crystalline products can  
13 be prepared. As is the case in most molecular sieve  
14 syntheses, a given template may not necessarily produce a  
15 crystalline product or a single molecular sieve over all  
16 inorganic composition ranges.  
17

18                   Example 12: ALPO reaction  
19

20 4.05 Grams of Catapal B (alumina source) were added with  
21 stirring to 6.84 grams of an 86% H<sub>3</sub>PO<sub>4</sub> solution over a 1-hour  
22 period. An additional 1 gram of water was added to aid in  
23 stirring, which was continued for 3 hours after the Catapal  
24 addition was complete. 1.81 Grams of this stock solution  
25 was transferred to a Teflon cup of a Parr 4745 reactor. A  
26 stir bar was added and 4.45 grams of a 0.56 M solution of  
27 the template of Example 7 as the hydroxide salt was added  
28 while stirring. The resultant thick white gel was stirred  
29 overnight at room temperature. The reactor was then heated  
30 to 150°C in a Blue M oven. After 48 hours, an increase in  
31 pH was noted and a settled product was obtained. The solids  
32 were filtered, washed with water, dried and determined by  
33 XRD to be ALPO-5.  
34

-35-

01

Example 13: ALPO reaction

02

03 The procedure of Example 12 was repeated, except that  
04 3.41 grams of a 0.73 M solution of the template from  
05 Example 2 as the hydroxide salt was used. After two days,  
06 the product isolated was ALPO-5.

07

08

Example 14: ALPO reaction

09

10 The procedure of Example 12 was repeated, except that  
11 4.05 grams of a 0.62 M solution of the template from  
12 Example 6 as the hydroxide salt was used. The product  
13 isolated was ALPO-5.

14

15

Example 15: ALPO reaction

16

17

18 The procedure of Example 12 was repeated, except that  
19 4.19 grams of a 0.59 M solution of the template from  
20 Example 10 as the hydroxide salt was used. The product  
isolated was ALPO-5.

21

22

Example 16: SAPO reaction

23

24

25 4.04 Grams of Catapal B were added with stirring to a  
mixture of 6.83 grams of an 86% H<sub>3</sub>PO<sub>4</sub> solution and  
26 10.00 grams of water over a period of one hour. The  
resulting gel was aged for one hour, after which was added  
27 0.37 grams of Cabosil M-5 fumed silica. 2.9 Grams of the  
28 resulting solution was transferred to a Teflon cup of a Parr  
29 4745 reactor, and 3.41 grams of a 0.734 M solution of the  
30 template from Example 2 (structure VII) was slowly added  
31 with stirring. The resulting reaction mixture was heated at  
32 150°C for 48 hours, after which a settled product was  
33 obtained. The solids were filtered, washed with water,

-36-

01 dried and determined by XRD to be SAPO-5 with a small amount  
02 of SAPO-34.

03

04 Example 17: SAPO reaction

05

06 The same reaction mixture as described in Example 16 was  
07 prepared, with the exception that the mixture was heated at  
08 170°C for 48 hours. The products from this reaction were  
09 determined by XRD to be SAPO-5 with a small amount of  
10 SAPO-34.

11

12 Example 18: SAPO reaction

13

14 The same reaction mixture as described in Example 16 was  
15 prepared, with the exception that 4.29 grams of a 0.58 M  
16 solution of the template prepared in Example 6  
17 (structure XI) as the hydroxide salt was used instead of the  
18 template from Example 2. After heating for 48 hours at  
19 150°C, a settled product was obtained and determined by XRD  
20 to be SAPO-5 with a trace amount of SAPO-34.

21

22 Example 19: SAPO reaction

23

24 The same reaction mixture as described in Example 16 was  
25 prepared, with the exception that 4.45 grams of a 0.56 M  
26 solution of the template prepared in Example 7  
27 (structure XII) as the hydroxide salt was used instead of  
28 the template from Example 2. After heating for 48 hours at  
29 150°C, a settled product was obtained and determined by XRD  
30 to be SAPO-5.

31

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-37-

01

Example 20: SAPO reaction

02

03 The same reaction mixture as described in Example 16 was  
04 prepared, with the exception that 3.83 grams of a 0.65 M  
05 solution of the template prepared in Example 1 (structure  
06 VI) as the hydroxide salt was used instead of the template  
07 from Example 2. After heating for 48 hours at 150°C, a  
08 settled product was obtained and determined by XRD to be a  
09 mixture of SAPO-5 and SAPO-34.

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-38-

01 WHAT IS CLAIMED IS:

02

03 1. A method for preparing a crystalline molecular sieve  
04 comprising oxides of one or more trivalent element(s)  
05 and oxides of one or more pentavalent element(s), said  
06 method comprising contacting under crystallization  
07 conditions one or more active sources of said oxides  
08 with a templating agent having a molecular structure of  
09 the form:

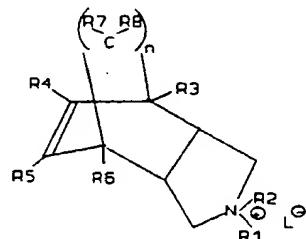
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14 (I)



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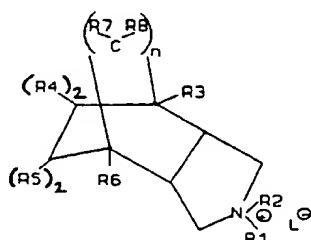
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21 (IA)



22

23

24

25 wherein:

26

27 R1 and R2 are at each independent occurrence  
28 selected from the group consisting of hydrogen, a  
29 lower alkyl group, and when taken together, a  
30 spirocyclic group having from 3 to 6 carbon atoms;

31

32 R3, R4, R5 and R6 are at each independent  
33 occurrence selected from the group consisting of  
34 hydrogen, halogen, and a lower alkyl group;

-39-

01        n has at each independent occurrence a value of 1,  
02        2, 3, or 4;

03

04        R7 and R8 are at each independent occurrence  
05        selected from the group consisting of hydrogen,  
06        and a lower alkyl group, and when n is one (1), R7  
07        and R8 can be taken together to form a spirocyclic  
08        group having from 3 to 6 carbon atoms; and when n  
09        is two (2) or greater, one of R7 and R8 on one  
10        carbon atom can be taken together with one of R7  
11        and R8 on an adjacent carbon atom to form a ring  
12        having from 3 to 6 carbon atoms; and

13

14        L is an anion which is not detrimental to the  
15        formation of the molecular sieve;

16

17        or a molecular structure of the form:

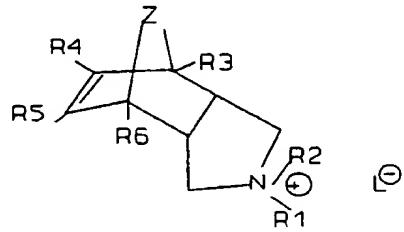
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(II)



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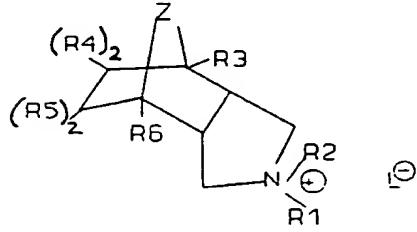
27

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(IIIA)



31

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-40-

01       wherein Z is at each independent occurrence selected  
02       from the group consisting of oxygen, nitrogen, sulfur,  
03       and a hydrocarbyl radical; and

04

05       R1, R2, R3, R4, R5, R6, and L are as defined above.

06

07       2. The method according to Claim 1 wherein R1 and R2 are  
08       each selected from the group consisting of hydrogen, an  
09       alkyl group having from 1 to 3 carbon atoms, and when  
10       taken together, a spirocyclic group having from 4 to 5  
11       carbon atoms.

12

13       3. The method according to Claim 1 wherein R3, R4, R5 and  
14       R6 are each selected from the group consisting of  
15       hydrogen and an alkyl group having from 1 to 3 carbon  
16       atoms.

17

18       4. The method according to Claim 1 wherein R7 and R8 are  
19       each selected from the group consisting of hydrogen,  
20       and an alkyl group having from 1 to 3 carbon atoms, and  
21       when n is one (1), R7 and R8 can be taken together to  
22       form a spirocyclic group having from 3 to 6 carbon  
23       atoms; and when n is two (2) or greater, one of R7 and  
24       R8 on one carbon atom can be taken together with one of  
25       R7 and R8 on an adjacent carbon atom to form a ring  
26       having from 3 to 6 carbon atoms.

27

28       5. The method according to Claim 1 wherein the templating  
29       agent has a molecular structure of the form:

30

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-41-

01

02

03

04

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07

08 wherein:

09

10 R1, R2, R3, R4, R5, R6 and L are as defined in  
11 Claim 1; and

12

13 R9 and R10 are each selected from the group  
14 consisting of hydrogen, a lower alkyl group, and  
15 when taken together, a spirocyclic group having  
16 from 3 to 6 carbon atoms.

17

18 6. The method according to Claim 5 wherein R1 and R2 are  
19 selected from the group consisting of hydrogen, an  
20 alkyl group having from 1 to 3 carbon atoms, and when  
21 taken together, a spirocyclic group having from 4 to 5  
22 carbon atoms.

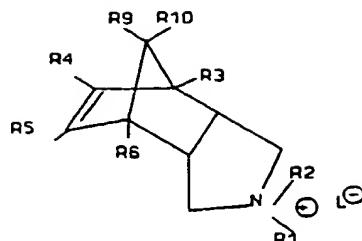
23

24 7. The method according to Claim 5 wherein R3, R4, R5 and  
25 R6 are each selected from the group consisting of  
26 hydrogen and an alkyl group having from 1 to 3 carbon  
27 atoms.

28

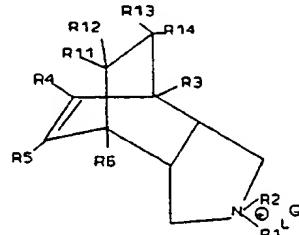
29 8. The method according to Claim 5 wherein R9 and R10 are  
30 each selected from the group consisting of hydrogen, an  
31 alkyl group having from 1 to 3 carbon atoms, and when  
32 taken together, a spirocyclic group having from 3 to 6  
33 carbon atoms.

34



-42-

01        9. The method according to Claim 5 wherein R3, R4, R5, R6,  
02                  R9, and R10 are the same and each is hydrogen.  
03  
04        10. The method of Claim 9 wherein R1 and R2 are the same  
05                  and each is methyl.  
06  
07        11. The method according to Claim 9 wherein R1 is methyl,  
08                  R2 is ethyl.  
09  
10        12. The method according to Claim 9 wherein R1 and R2 are  
11                  the same and each is ethyl.  
12  
13        13. The method according to Claim 5 wherein R1 and R2 are  
14                  the same and each is methyl, and R3, R4, R5, and R6,  
15                  are the same and each is hydrogen, and R9 and R10 are  
16                  taken together to form a spirocyclic cyclopropane ring.  
17  
18        14. The method according to Claim 13 wherein R1 and R2 are  
19                  the same and each is ethyl.  
20  
21        15. The method according to Claim 1 wherein the templating  
22                  agent has a molecular structure of the form:  
23  
24  
25  
26  
27  
28  
29  
30  
31                  wherein:



32  
33                  R1, R2, R3, R4, R5, R6 and L are as defined in  
34                  Claim 1; and

-43-

01            R11, R12, R13, and R14 are each selected from the  
02            group consisting of hydrogen, and a lower alkyl  
03            group.

04

05        16. The method according to Claim 15 wherein R1 and R2 are  
06            selected from the group consisting of hydrogen, an  
07            alkyl group having from 1 to 3 carbon atoms, and when  
08            taken together, a spirocyclic group having from 4 to 5  
09            carbon atoms.

10

11        17. The method according to Claim 15 wherein R3, R4, R5 and  
12            R6 are each selected from the group consisting of  
13            hydrogen and an alkyl group having from 1 to 3 carbon  
14            atoms.

15

16        18. The method according to Claim 15 wherein R11, R12, R13,  
17            and R14 are each selected from the group consisting of  
18            hydrogen, and an alkyl group having from 1 to 3 carbon  
19            atoms.

20

21        19. The method according to Claim 15 wherein R3, R4, R5,  
22            and R6 are the same and each is hydrogen.

23

24        20. The method according to Claim 19 wherein R11, R12, R13,  
25            and R14 are the same and each is hydrogen.

26

27        21. The method according to Claim 20 wherein R1 and R2 are  
28            the same and each is methyl.

29

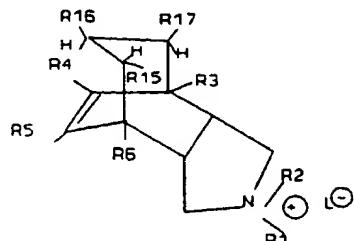
30        22. The method according to Claim 20 wherein R1 is methyl  
31            and R2 is ethyl.

32

33        23. The method according to Claim 20 wherein R1 and R2 are  
34            the same and each is ethyl.

-44-

01 24. The method according to Claim 1 wherein the templating  
02 agent has a molecular structure of the form:



wherein:

R1, R2, R3, R4, R5, R6 and L are as defined in  
Claim 1; and

R15, R16, and R17 are each selected from the group  
consisting of hydrogen, and a lower alkyl group.

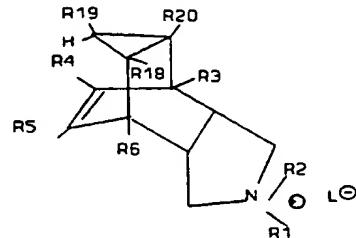
25. The method according to Claim 24 wherein R1 and R2 are  
selected from the group consisting of hydrogen, an  
alkyl group having from 1 to 3 carbon atoms, and when  
taken together, a spirocyclic group having from 4 to 5  
carbon atoms.

26. The method according to Claim 24 wherein R3, R4, R5 and  
R6 are each selected from the group consisting of  
hydrogen and an alkyl group having from 1 to 3 carbon  
atoms.

27. The method according to Claim 24 wherein R15, R16, and  
R17 are each selected from the group consisting of  
hydrogen, and an alkyl group having from 1 to 3 carbon  
atoms.

-45-

01 28. The method according to Claim 24 wherein R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>,  
02 and R<sub>6</sub> are the same and each is hydrogen.  
03  
04 29. The method according to Claim 28 wherein R<sub>15</sub>, R<sub>16</sub>, and  
05 R<sub>17</sub> are the same and each is hydrogen.  
06  
07 30. The method according to Claim 29 wherein R<sub>1</sub> and R<sub>2</sub> are  
08 the same and each is methyl.  
09  
10 31. The method according to Claim 29 wherein R<sub>1</sub> is methyl  
11 and R<sub>2</sub> is ethyl.  
12  
13 32. The method according to Claim 1 wherein the templating  
14 agent has a molecular structure of the form:  
15  
16



22  
23 wherein:

24  
25 R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and L are as defined in  
26 Claim 1; and  
27  
28 R<sub>18</sub>, R<sub>19</sub>, and R<sub>20</sub> are each selected from the group  
29 consisting of hydrogen, and a lower alkyl group.  
30  
31 33. The method according to Claim 32 wherein R<sub>1</sub> and R<sub>2</sub> are  
32 selected from the group consisting of hydrogen, an  
33 alkyl group having from 1 to 3 carbon atoms, and when  
34

-46-

01        taken together, a spirocyclic group having from 4 to 5  
02        carbon atoms.

03

04        34. The method according to Claim 32 wherein R3, R4, R5 and  
05        R6 are each selected from the group consisting of  
06        hydrogen and an alkyl group having from 1 to 3 carbon  
07        atoms.

08

09        35. The method according to Claim 32 wherein R18, R19, and  
10        R20 are each selected from the group consisting of  
11        hydrogen, and an alkyl group having from 1 to 3 carbon  
12        atoms.

13

14        36. The method according to Claim 32 wherein R3, R4, R5,  
15        and R6 are the same and each is hydrogen.

16

17        37. The method according to Claim 36 wherein R18, R19, and  
18        R20 are the same and each is hydrogen.

19

20        38. The method according to Claim 37 wherein R1 and R2 are  
21        the same and each is methyl.

22

23        39. The method according to Claim 1 wherein L is selected  
24        from the group consisting of fluoride, chloride,  
25        bromide, iodide, hydroxide, acetate, sulfate, and  
26        carboxylate.

27

28        40. The method according to Claim 39 wherein L is  
29        hydroxide.

30

31        41. The method according to Claim 1 wherein the trivalent  
32        element is aluminum.

33

34

-47-

01 42. The method according to Claim 1 wherein the pentavalent  
02 element is phosphorous.

03

04 43. The method according to Claim 1 wherein the crystalline  
05 molecular sieve further comprises an oxide of one or  
06 more tetravalent element(s).

07

08 44. The method according to Claim 43 wherein the  
09 tetravalent element is silicon.

10

11 45. A method for preparing a crystalline molecular sieve  
12 having a three-dimensional microporous framework  
13 structure comprising  $[AlO_2]$  and  $[PO_2]$  oxide units, said  
14 method comprising contacting sources of said oxide  
15 unites and a templating agent having a molecular  
16 structure of the form:

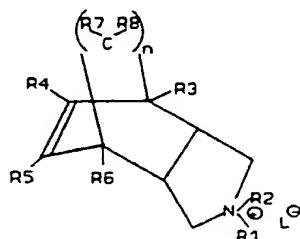
17

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19

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(I)



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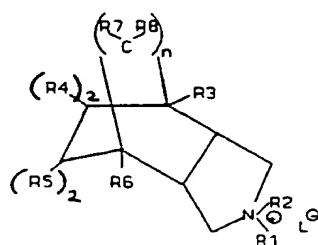
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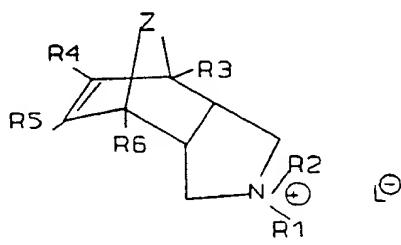
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wherein:

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-48-

01 R1 and R2 are at each independent occurrence  
02 selected from the group consisting of hydrogen, a  
03 lower alkyl group, and when taken together, a  
04 spirocyclic group having from 3 to 6 carbon atoms;  
05  
06 R3, R4, R5 and R6 are at each independent  
07 occurrence selected from the group consisting of  
08 hydrogen, halogen, and a lower alkyl group;  
09  
10 n has at each independent occurrence a value of 1,  
11 2, 3, or 4;  
12  
13 R7 and R8 are at each independent occurrence  
14 selected from the group consisting of hydrogen,  
15 and a lower alkyl group, and when n is one (1), R7  
16 and R8 can be taken together to form a spirocyclic  
17 group having from 3 to 6 carbon atoms; and when n  
18 is two (2) or greater, one of R7 and R8 on one  
19 carbon atom can be taken together with one of R7  
20 and R8 on an adjacent carbon atom to form a ring  
21 having from 3 to 6 carbon atoms; and  
22  
23 L is an anion which is not detrimental to the  
24 formation of the molecular sieve;  
25 or a molecular structure of the form:  
26  
27  
28  
29  
30 (II)



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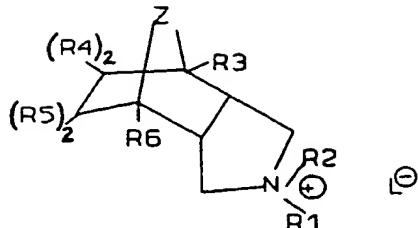
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(IIA)



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09       wherein Z is at each independent occurrence selected  
10      from the group consisting of oxygen, nitrogen, sulfur,  
11      and an alkylene radical; and

12

13      R1, R2, R3, R4, R5, R6, and L are as defined above.

14

15      46. The method according to Claim 45 wherein the framework  
16      structure further comprises an oxide of at least one  
17      element other than aluminum and phosphorous which is  
18      capable of forming an oxide in tetrahedral coordination  
19      with  $[AlO_2]$  and  $[PO_2]$  oxide structural units in a  
20      crystalline molecular sieve.

21

22      47. The method according to Claim 46 wherein the element  
23      other than aluminum and phosphorous is selected from  
24      the group consisting of arsenic, beryllium, boron,  
25      chromium, cobalt, gallium, germanium, iron, lithium,  
26      magnesium, manganese, silicon, titanium, vanadium, and  
27      zinc.

28

29      48. The method according to Claim 46 wherein the element is  
30      selected from the group consisting of silicon,  
31      magnesium, manganese, cobalt, and zinc.

32

33      49. The method according to Claim 46 wherein the element is  
34      silicon.

-50-

01 50. The method according to Claim 45 wherein the molecular  
02 sieve is AlPO<sub>4</sub>-5.

03

04 51. A crystalline molecular sieve comprising oxides of one  
05 or more trivalent element(s) and of one or more  
06 pentavalent element(s), and having therein the  
07 templating agent of Claim 1.

08

09 52. The crystalline molecular sieve of Claim 51 having a  
10 molar composition, as synthesized and in the anhydrous  
11 state, as follows:

12

13                           aQ: (M<sub>x</sub>Al<sub>y</sub>P<sub>z</sub>) O<sub>2</sub>

14

15                           wherein:

16

17                           Q is the templating agent;

18

19                           a has a value in the range of greater than zero  
20 and no greater than about 0.3;

21

22                           M is one or more elements capable of forming  
23                           stable M--O--P, M--O--Al, or M--O--M bonds in  
24                           crystalline oxide structures;

25

26                           y and z each have a value of at least 0.01; and

27

28                           the sum of x, y, and z is 1.

29

30 53. The composition according to Claim 52 wherein x has a  
31                           value equal to zero.

32

33 54. The composition according to Claim 52 wherein element M  
34                           is selected from the group consisting of arsenic,

-51-

01        beryllium, boron, chromium, cobalt, gallium, germanium,  
02        iron, lithium, magnesium, manganese, silicon, titanium,  
03        vanadium, and zinc.

04

05        55. The composition according to Claim 54 wherein element M  
06        is selected from the group consisting of magnesium,  
07        manganese, cobalt, and zinc.

08

09        56. The composition according to Claim 55 wherein element M  
10        is silicon.

11

12        57. The process of thermally treating the crystalline  
13        molecular sieve of Claim 51 at a temperature of about  
14        200°C to about 800°C.

15

16        58. The process of thermally treating the crystalline  
17        molecular sieve of Claim 52 at a temperature of about  
18        200°C to about 800°C.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/01402

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C01B 37/04, 37/06

US CL :423/706, 708, Dig 30; 502/208, 214

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/706, 708, Dig 30; 502/208, 214

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	US, A, 5,340,563 (Zones et al.) 23 August 1994.	
A	US, A, 5,281,407 (Nakagawa) 25 January 1994.	
A	US, A, 5,268,161 (Nakagawa) 7 December 1993.	
A	US, A, 5,254,514 (Nakagawa) 19 October 1993.	
A	US, A, 5,225,179 (Zones et al.) 6 July 1993.	
A	US, A, 4,793,984 (Lok et al.) 27 December 1988.	
A	US, A, 4,440,871 (Lok et al.) 3 April 1984.	

 Further documents are listed in the continuation of Box C. See patent family annex.

*A*	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

04 MARCH 1995

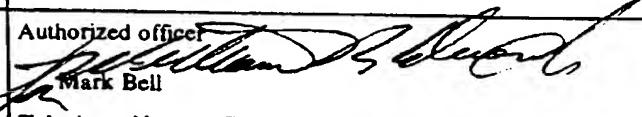
Date of mailing of the international search report

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Name and mailing address of the ISA/US  
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